



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Tsukasa Fujieda ) Group Art Unit:  
Appl. No. : 10/576,193 ) 1792  
)  
Filed : April 17, 2006 ) Examiner:  
)  
For : METHOD OF FORMING LUSTER )  
COATING FILM )

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DECLARATION UNDER 37 C.F.R. §1.132

Commissioner for Patents  
PO Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

I, Tsukasa Fujieda, do hereby declare that:

1. I am one of the inventors of the above-identified application.
2. I graduated from Kobe Design University, Faculty of Design, Department of Visual Communication Design in Mar. 1993. In Apr. 1993, I joined KANSAI PAINT Co., Ltd., assignee of the above-identified application, where I have been engaged in research on color development from Apr. 1993 to the present.

Since Apr. 1994, I have been engaged in research on color development as an engineer in the CD laboratory of KANSAI PAINT Co., Ltd.

3. The experiments given below were carried out under my general direction and supervision.

### Experiment

#### 1. Summary and Purpose of Experiment

A method comprising repeating a step of applying a base coating composition and a step of applying a clear coating composition, and a method in which each of the above steps is not repeated, are conducted with a variety of thicknesses of the base coating composition applied, and with a variety of the number of stages of applying the base coating composition. Each of the obtained coating films was evaluated for density of texture and flip-flop property.

In each example, parts and percentages are by weight.

#### 2. Experimental Methods

Preparation of an aqueous luster thermosetting base coating composition and clear coating composition

Production of acrylic resin emulsion

Production Example 1

One hundred and forty parts of deionized water, 2.5

parts of a 30% aqueous solution of a surfactant (tradename "Newcol 707SF", product of Nippon Nyukazai Co., Ltd.) and 1 part of the monomer mixture (1) shown below were placed in a reactor and mixed by stirring under a nitrogen stream, followed by the addition of 3 parts of 3% ammonium persulfate at 60°C. The resulting mixture was then heated to 80°C, and a monomer emulsion consisting of 79 parts of monomer mixture (1), 2.5 parts of a 30% aqueous solution of a surfactant (tradename "Newcol 707SF", product of Nippon Nyukazai Co., Ltd.), 4 parts of 3% ammonium persulfate and 42 parts of deionized water was added to the reactor over 4 hours using a metering pump. After addition, the resulting mixture was aged for 1 hour.

Further, 20.5 parts of the monomer mixture (2) shown below and 4 parts of a 3% aqueous solution of ammonium persulfate were added concurrently and dropwise to the reactor over 1.5 hours. After addition, the resulting mixture was aged for 1 hour, diluted with 30 parts of deionized water and filtered through 200-mesh nylon cloth at 30°C. Deionized water was further added to the filtrate, and the pH was adjusted to 7.5 with dimethylaminoethanolamine to thereby obtain an acrylic resin emulsion with a mean particle size of 0.1  $\mu\text{m}$  and a solids content of 20%. The acrylic resin had a hydroxy value of 15 mgKOH/g.

Monomer mixture (1): a mixture of 55 parts of methyl methacrylate, 8 parts of styrene, 9 parts of n-butyl acrylate, 5 parts of 2-hydroxyethyl acrylate, 2 parts of 1,6-hexanediol

diacrylate and 1 part of methacrylic acid.

Monomer mixture (2): a mixture of 5 parts of methyl methacrylate, 7 parts of n-butyl acrylate, 5 parts of 2-ethylhexyl acrylate, 3 parts of methacrylic acid and 0.5 parts of a 30% aqueous solution of a surfactant (tradename "Newcol 707SF", product of Nippon Nyukazai Co., Ltd.).

#### Production of polyurethane resin emulsion

##### Production Example 2

In a polymerization reactor, 115.5 parts of polybutylene adipate with a number average molecular weight of 2,000, 115.5 parts of polycaprolactone diol with a number average molecular weight of 2,000, 23.2 parts of dimethylolpropionic acid, 6.5 parts of 1,4-butanediol and 120.1 parts of 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane were placed and reacted while stirring in a nitrogen gas atmosphere at 85°C for 7 hours to obtain an NCO-terminated prepolymer with an NCO content of 4.0%.

The prepolymer was then cooled to 50°C, and 165 parts of acetone was added to form a homogeneous solution. While stirring, 15.7 parts of triethylamine was added, and 600 parts of ion exchange water was added while maintaining the temperature of 50°C or lower. After maintaining the temperature at 50°C for 2 hours to complete the water extension reaction, the acetone was distilled off under reduced pressure at 70°C to obtain a polyurethane resin emulsion with a solids

content of 42%.

#### Preparation of crosslinking agent

##### Production Example 3

(1) Sixty parts of ethylene glycol monobutyl ether and 15 parts of isobutyl alcohol were placed in a reactor, and heated to 115°C under a nitrogen stream. When the mixture had been heated to 115°C, a mixture of 26 parts of n-butyl acrylate, 47 parts of methyl methacrylate, 10 parts of styrene, 10 parts of 2-hydroxyethyl methacrylate, 6 parts of acrylic acid and 1 part of azoisobutyronitrile was added over 3 hours. After completion of addition, aging was performed at 115°C for 30 minutes, and a mixture of 1 part of 2,2'-azobisisobutyronitril and 115 parts of ethylene glycol monobutyl ether was added over 1 hour. After aging for 30 minutes, the resulting mixture was filtered through 200-mesh nylon cloth at 50°C. The obtained reaction product had an acid value of 48 mgKOH/g, a viscosity of Z<sub>4</sub> (Gardner bubble viscometer) and a nonvolatile content of 55%. The reaction product was neutralized with an equivalent amount of dimethylaminoethanol, followed by the addition of deionized water, to obtain a 50% aqueous solution of an acrylic resin.

(2) In a stirring container, 41.7 parts of butyl etherified melamine resin (tradename "U-Van 28SE", product of Mitsui Chemicals, Inc., nonvolatile content: 60%) was placed as a hydrophobic melamine resin, and 20 parts of the aqueous acrylic resin solution obtained in (1) above was added. Eighty

parts of deionized water was gradually added while stirring with an agitating blade mixer at an rpm of 1,000 to 1,500. Stirring was continued for another 30 minutes to thereby obtain an aqueous dispersion of a crosslinking agent with a solids content of about 20% and a mean particle diameter of 0.11  $\mu\text{m}$ .

Production of aqueous luster thermosetting base coating composition (A)

Production Example 4

Three hundred and twenty five parts of the acrylic resin emulsion with a solids content of 20% obtained in Production Example 1, 35.7 parts of the polyurethane resin emulsion with a solids content of 42% obtained in Production Example 2, and 100 parts of the crosslinking agent dispersion with a solids content of 20% obtained in Production Example 3 were mixed. Twenty-six parts of paste-form aluminum flake pigment (tradename "Alpaste MH-6601"; product of Asahi Chemical Industry Co., Ltd.; a paste with a pigment content of 65%, comprising aluminum flakes with a mean particle diameter of 14.5  $\mu\text{m}$ , a mean thickness of 0.21  $\mu\text{m}$  and a mean particle diameter/mean thickness ratio of 70, the aluminum flakes being dispersed in a petroleum solvent) was further added, followed by mixing. The resulting mixture was adjusted to a solids content of 15% with deionized water to obtain aqueous luster thermosetting base coating composition (A-1) (hereunder simply referred to as "base coating composition (A-1)").

## Production of thermosetting clear coating composition (B)

### Production Example 5

(1) A monomer mixture of 20 parts of acrylic acid, 20 parts of styrene, 40 parts of n-butyl acrylate and 20 parts of 4-hydroxy n-butyl acrylate was copolymerized in a standard manner to obtain a carboxy- and hydroxy-containing acrylic resin with a number average molecular weight of 3,500, acid value of 86 mgKOH/g and hydroxy value of 78 mgKOH/g.

(2) A monomer mixture of 30 parts of glycidyl methacrylate, 20 parts of 4-hydroxy n-butyl acrylate, 40 parts of n-butyl acrylate and 20 parts of styrene was copolymerized in a standard manner to obtain an epoxy- and hydroxy-containing acrylic resin with a number average molecular weight of 3,000, epoxy content of 2.1 mmol/g and hydroxyl value of 78 mgKOH/g.

(3) A mixture of 50 parts of the carboxy- and hydroxy-containing acrylic resin obtained (1) above, 50 parts of the epoxy- and hydroxy-containing acrylic resin obtained in (2) above, 1 part of an ultraviolet absorber (tradename "Tinuvin 900", product of Ciba-Geigy), 1 part of tetrabutylammonium bromide and 0.1 part of a surface conditioner (tradename "BYK-300", product of BYK-Chemie) was diluted with an aromatic hydrocarbon solvent (tradename "Swasol #1000", product of Cosmo Oil Co., Ltd.) to adjust the viscosity to 20 seconds (Ford cup #4, 20°C) and thereby obtain thermosetting clear coating composition (B-1).

### Production of substrate

#### Production Example 6

A cationic electrodeposition coating composition (tradename "Elecron 9400HB", product of Kansai Paint Co., Ltd.) was applied by electrodeposition to a degreased and zinc phosphate-treated steel sheet to a thickness of 25  $\mu\text{m}$  (when cured), and heat-cured at 170°C for 20 minutes. A polyester resin-based intermediate coating composition (tradename "Amilac Intermediate Coat, Gray", product of Kansai Paint Co., Ltd.) was applied by air spraying to the cured electrodeposition coating to a thickness of 35  $\mu\text{m}$  (when cured), heat-cured at 140°C for 20 minutes to obtain a substrate having an electrodeposition coating and intermediate coating.

#### Experiment 1

Aqueous luster base coating composition (A-1) obtained in Production Example 4 was applied in two stages to the substrate obtained in Production Example 6, using a Metabell rotary electrostatic coater at 30,000 rpm, shaping pressure of 1.7 kg/cm<sup>2</sup>, gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%, in such a manner that the thickness of the coating composition applied in each stage became about 3.5  $\mu\text{m}$  (when cured) and the total thickness of the coating composition applied in the two stages became 7  $\mu\text{m}$  (when cured). The applied coating composition was allowed to stand for 1 minute between the stages. The solids content of the applied composition one minute after the application in each stage was 50%.



After the two stages of application, the applied composition was allowed to stand for 3 minutes and preheated at 80°C for 10 minutes. Clear coating composition (B-1) was applied over the uncured coating layer of base coating composition (A-1) to a thickness of 30  $\mu\text{m}$  (when cured), using a Minibell rotary electrostatic coater at 30,000 rpm, shaping pressure of 1.5  $\text{kg}/\text{cm}^2$ , gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%, allowed to stand for 7 minutes, and heated at 140°C for 30 minutes to simultaneously cure the two uncured coating layers of base coating composition (A-1) and clear coating composition (B-1).

Aqueous luster base coating composition (A-1) was applied in two stages over the cured coating layer of clear coating composition (B-1) using a Metabell rotary electrostatic coater at 30,000 rpm, shaping pressure of 1.7  $\text{kg}/\text{cm}^2$ , gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75°C, in such a manner that the thickness of the coating composition applied in each stage became about 3.5  $\mu\text{m}$  (when cured) and the total thickness of the coating composition applied in the two stages became 7  $\mu\text{m}$  (when cured). The applied coating composition was allowed to stand for 1 minute between the stages. The solids content of the applied composition one minute after the application in each stage was 50%.

After the two stages of application, the applied composition was allowed to stand for 3 minutes, and preheated

at 80°C for 10 minutes. Clear coating composition (B-1) was applied over the uncured coating layer of base coating composition (A-1) to a thickness of 30  $\mu\text{m}$  (when cured), using a Minibell rotary electrostatic spray coater at 30,000 rpm, shaping pressure of 1.5  $\text{kg}/\text{cm}^2$ , gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%, allowed to stand for 7 minutes and heated at 140°C for 30 minutes to simultaneously cure the two uncured coating layers of base coating composition (A-1) and clear coating composition (B-1).

A coated sheet was thus obtained in which a luster multilayer coating film was formed on a substrate by a four-coat two-bake method.

#### Experiment 2

Aqueous luster base coating composition (A-1) obtained in Production Example 4 was applied in two stages to the substrate obtained in Production Example 6, using a Metabell rotary electrostatic coater at 30,000 rpm, shaping pressure of 1.7  $\text{kg}/\text{cm}^2$ , gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%, in such a manner that the thickness of the coating composition applied in the first stage became about 5  $\mu\text{m}$  (when cured), the thickness of the coating composition applied in the second stage became about 2.5  $\mu\text{m}$  (when cured), and the total thickness of the coating composition applied in the two stages became 7.5  $\mu\text{m}$  (when cured). The applied coating composition was allowed to stand for 1 minute between the stages. The solids content of the applied

composition one minute after the application in the first stage was 45%. The solids content of the applied composition one minute after the application in the second stage was 60%.

After the two stages of application, the applied composition was allowed to stand for 3 minutes and preheated at 80°C for 10 minutes. Clear coating composition (B-1) was applied over the uncured coating layer of base coating composition (A-1) to a thickness of 30  $\mu\text{m}$  (when cured), using a Minibell rotary electrostatic coater at 30,000 rpm, shaping pressure of 1.5  $\text{kg}/\text{cm}^2$ , gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%, allowed to stand for 7 minutes and heated at 140°C for 30 minutes to simultaneously cure the two uncured coating layers of base coating composition (A-1) and clear coating composition (B-1).

Aqueous luster base coating composition (A-1) was applied in two stages over the cured coating layer of clear coating composition (B-1), using a Metabell rotary electrostatic coater at 30,000 rpm, shaping pressure of 1.7  $\text{kg}/\text{cm}^2$ , gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75°C, in such a manner that the thickness of the coating composition applied in each stage became about 2.5  $\mu\text{m}$  (when cured) and the total thickness of the coating composition applied in the two stages became 5  $\mu\text{m}$  (when cured). The applied coating composition was allowed to stand for 1 minute between the stages. The solids contents of the applied composition one minute after the application in the first and

second stages were each 60%. After the two stages of application, the applied composition was allowed to stand for 3 minutes, and preheated at 80°C for 10 minutes. Clear coating composition (B-1) was applied over the uncured coating layer of base coating composition (A-1) to a thickness of 30  $\mu\text{m}$  (when cured) using a Minibell rotary electrostatic spray coater at 30,000 rpm, shaping pressure of 1.5 kg/cm<sup>2</sup>, gun distance of 30 cm, booth temperature of 20°C and booth humidity of 75%. The applied composition was allowed to stand for 7 minutes, and heating was performed at 140°C for 30 minutes to simultaneously cure the two uncured coating layers of base coating composition (A-1) and clear coating composition (B-1).

A coated sheet was thus obtained in which a luster multilayer coating film was formed on a substrate by a four-coat two-bake method.

#### Experiment 3

The procedure of Experiment 1 was followed except that each of the first and third coating layers was formed by applying aqueous luster base coating composition (A-1) in a single stage to a thickness of about 7  $\mu\text{m}$  (when cured), to obtain a coated sheet in which a luster multilayer coating film was formed on a substrate by a four-coat two-bake method.

#### Experiment 4

Aqueous luster base coating composition (A-1) was applied in two stages to the substrate obtained in Production Example 6, using a Metabell rotary electrostatic coater at

30,000 rpm, shaping pressure of  $1.7 \text{ kg/cm}^2$ , gun distance of 30 cm, booth temperature of  $20^\circ\text{C}$  and booth humidity of 75%, in such a manner that the thickness of the coating composition applied in the each stage became about  $6 \mu\text{m}$  (when cured), and the total thickness of the coating composition applied in the two stages became  $12 \mu\text{m}$  (when cured). The applied coating composition was allowed to stand for 1 minute between the stages. The solids contents of the applied composition one minute after the application in the first and second stages were each 40%.

After the two stages of application, the applied composition was allowed to stand for 3 minutes and preheated at  $80^\circ\text{C}$  for 10 minutes. Clear coating composition (B-1) was applied to the uncured coating layer of base coating composition (A-1) to a thickness of  $30 \mu\text{m}$  (when cured), using a Minibell rotary electrostatic spray coater at 30,000 rpm, shaping pressure of  $1.5 \text{ kg/cm}^2$ , gun distance of 30 cm, booth temperature of  $20^\circ\text{C}$ , and booth humidity of 75%. The applied composition was allowed to stand for 7 minutes, and heating was performed at  $140^\circ\text{C}$  for 30 minutes to simultaneously cure the two uncured coating layers of base coating composition (A-1) and clear coating composition (B-1).

A coated sheet was thus obtained in which a luster multilayer coating film was formed on a substrate by a two-coat one-bake method.

#### Experiment 5

The procedure of Experiment 4 was followed except

that base coating composition (A-1) was applied in three stages, in such a manner that the thickness of the coating composition applied in each stage became about 8  $\mu\text{m}$  (when cured), about 4  $\mu\text{m}$  (when cured), and about 4  $\mu\text{m}$  (when cured), to obtain a coated sheet in which a luster multilayer coating film was formed on a substrate by a two-coat one-bake method.

#### Performance evaluation tests

The coated sheets obtained in Experiments 1 to 5 were tested for density of texture and flip-flop property by the following methods.

Density of texture: The highlight of the coating surface of each coated sheet was observed by the naked eye, and evaluated according to the following criteria. A: The coating surface was only slightly grainy and had a highly dense texture; B: The coating surface was very grainy and had a poor density of texture.

As another evaluation of the density of texture, the HG (Highlight Graininess) value of the coating surface of each coated sheet was measured using a micro-brilliance measuring instrument (product of Kansai Paint Co., Ltd.). The micro-brilliance measuring instrument is equipped with a light source, a CCD (Charge Coupled Device) camera and an image analyzer, and is disclosed in Japanese Unexamined Patent Publication No. 2001-221690.

The HG value is a parameter of micro-brilliance obtained by the microscopic observation of a coating surface,

and indicates the graininess of the highlight of the coating surface. The HG value is calculated as follows.

First, the coating surface is photographed with a CCD camera at a light incidence angle of  $15^\circ$  and receiving angle of  $0^\circ$ , and the obtained digital image data (two-dimensional brilliance distribution data) is subjected to two-dimensional Fourier transformation to obtain a power spectrum image. Subsequently, the spatial frequency area corresponding to graininess is extracted from the power spectrum image, and the obtained measurement parameter is converted to an HG value from 0 to 100 that has a linear relation with graininess.

An HG value of 0 indicates no graininess of the luster pigment at all, and an HG value of 100 indicates the highest possible graininess of the luster pigment.

Flip-flop property: The highlight and shade of the coating surface of each coated sheet were observed by the naked eye, and evaluated according to the following criteria. A: A large difference in brightness between the highlight and shade; B: A small difference in brightness between the highlight and shade; C: Almost no difference in brightness between the highlight and shade.

Further, using a multi-angle spectrophotometer (tradename "MA68II", product of X-Rite in the U.S.), the color of the coating surface of each coated sheet was determined, and the reflectance at receiving angles of  $15^\circ$  and  $110^\circ$  from the regular reflection light was measured at a light incidence

angle of 45°. The ratio of the reflectance at a receiving angle of 15° to that at a receiving angle of 110° (FF value) was calculated. The higher the FF value, the higher the flip-flop property.

### 3. Results

Table 1 shows the results of the evaluation tests of density of texture and flip-flop property.

[Table 1]

Experiment		1	2	3	4	5
Density of texture	Naked eye observation	A	A	B	B	B
	HG value	45	48	55	57	58
Flip-flop property	Naked eye observation	A	A	B	C	C
	FF value	1.8	1.8	1.5	1.3	1.3

### 4. Analysis

The coating film obtained by the method comprising repeating the step of applying an aqueous luster thermosetting base coating composition (steps (1) and (3)), and the step of applying a thermosetting clear coating composition (steps (2) and (4)), wherein in steps (1) and (3), the aqueous luster thermosetting base coating composition is applied in two to five stages, in such a manner that the thickness of the base coating composition applied in each stage becomes 0.3 to 5  $\mu$ m when cured (Experiments 1 and 2), showed a highly dense texture and



excellent flip-flop property.

Comparatively, when the base coating composition was applied in three stages at each thickness of 8  $\mu\text{m}$ , 4  $\mu\text{m}$  and 4  $\mu\text{m}$ , and the step of applying the base coating composition and the step of applying the clear coating composition were not repeated (Experiment 5), although the thicknesses of the base coating composition applied in the second and third stages were relatively as thin as 4  $\mu\text{m}$ , the obtained coating film showed significantly inferior dense texture and flip-flop property.

Experiment 3 is different from Experiment 4 in that each of the base coating composition and the clear coating composition was repeatedly applied over a coating film consisting of base coating composition layers and clear coating composition layers; however, the coating film obtained in Experiment 3 showed only a slight improvement in the dense texture and flip-flop property.

Experiment 5 is different from Experiment 4 in that the number of the stages of applying the base coating composition was increased from two to three, and the thicknesses of the coating composition applied in the second and third stages were made thinner; however, the results of the flip-flop property showed no difference, and the dense texture was an undesirably high value.

I, the undersigned, declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: March 5, 2010

Tsukasa Fujieda

Tsukasa Fujieda